Hydrogen Technical Analysis: Evaluation of Metal Hydride Slurries

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Objectives

- Assess the potential economic, environmental, and other benefits of using metal hydride slurries in a small-scale hydrogen distribution system (H_2 mini-grid) for both hydrogen vehicle fueling (H_2 station) and proton exchange membrane (PEM) fuel cell power systems (FCPSs) for combined building heat and power (cogen).
- Assess the viability of using fluorinated (or otherwise treated) metal hydrides for the purification of carbon monoxide (CO)-containing hydrogen streams.
- Establish R&D objectives for the development of hydrogen purification and H_2 mini-grids using metal hydride slurries.

Technical Barriers

This project addresses the following technical barriers from the following sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

Production

- AB.Hydrogen Separation and Purification
- AD.Market and Delivery

Delivery

- A. Lack of Hydrogen/Carrier and Infrastructure Options Analysis
- E. Solid and Liquid Hydrogen Carrier Transport

Storage

- V. Life Cycle and Efficiency Analysis

Approach

- Develop conceptual designs and evaluate the cost and efficiency of metal hydride slurry-based purification, storage, and delivery for H_2 stations and direct hydrogen FCPSs and compare to conventional systems (i.e. pressure swing adsorption purification, compressed hydrogen storage/ delivery, and reformate-based FCPSs).
- Determine cost of electricity (COE), hydrogen costs, energy use, greenhouse gas (GHG) emissions, and other emissions for FCPSs and H_2 stations utilizing both conventional and metal hydride slurry technology.
- Perform a molecular-level theoretical evaluation of the long-term feasibility of fluorinated metal hydride purification.

- Search for alternative protection methods or compounds that are even more effective in a practical application.

Accomplishments

- Developed conceptual designs and estimated capital costs for compressed hydrogen (cH_2)-based mini-grids and FCPSs.
- Constructed FCPS performance model with various building load profiles and FCPS efficiency calculations as inputs.
- Developed overall cost assessment and determined preliminary annual costs for reformate and direct hydrogen FCPSs.
- Integrated Phase I conceptual designs and capital costs for cH_2- and metal hydride slurry-based H_2 stations into FCPS performance model and overall cost assessment.

Future Directions

- Develop conceptual designs, evaluate efficiency, and estimate capital costs for metal hydride slurry-based mini-grids and FCPSs.
- Update FCPS performance model for metal hydride slurry-based systems.
- Refine capital cost estimates and evaluate hydrogen distribution costs for both cH_2- and metal hydride slurry-based mini-grids on a $/kg basis.
- Refine capital cost estimates and evaluate COE for cH_2-, reformate-, and metal hydride slurry-based FCPSs.
- Compare hydrogen costs, energy use, GHGs, and other emissions for the FCPS, H_2 mini-grid, and H_2 station utilizing both conventional and metal hydride slurry technologies.
- Evaluate other benefits of distributed generation and H_2 mini-grids.
- Use molecular modeling to describe a fluorinated layer of metal hydride on top of the virgin hydride.
- Establish selectivity of CO/H_2 separation based on energy surface calculation for transport through the fluorinated layer.
- Use the results to determine viability of fluorinated hydrides and develop and test hypothesis for optimization of the barrier layer.

Introduction

In Phase I, completed last year, the professionals at TIAX evaluated the potential cost and performance improvements that alternative and incipient hydrogen purification technologies could have over conventional pressure swing adsorption (PSA). The analysis indicated that the use of fluorinated metal hydrides in slurry form could reduce hydrogen cost and improve safety over conventional PSA purification with compressed hydrogen (cH_2) storage (Lasher et al 2002). In addition, if waste heat could be used to provide the heat for hydrogen desorption, metal hydride slurries could result in efficiency benefits. However, current metal hydrides have low tolerance to impurities typically found in reformate streams, especially oxygen and carbon monoxide. In Phase I, based on research results from Japan (Wang et al 1995a,b), we assumed that fluorinated (or in some other way protected) metal hydrides would be able to demonstrate high tolerance to impurities. However, significant additional research is required to verify these results and develop a stable and effective protective layer on the metal hydride.

Metal hydride slurry is a suspension of a metal hydride in an inert liquid, such as a light mineral oil or liquid alkane. The slurry is assumed to have no impact on the intrinsic hydride performance (e.g.

hydrogen capacity, hydrogen uptake kinetics, thermodynamics), but can result in overall system-level improvements such as higher heat transfer rates, easier transport (i.e. pump-able), and lower risk of impurities poisoning due to the liquid/gas equilibrium constant. A promising application identified for metal hydride slurries was combined purification, storage, and distribution in a small-scale hydrogen distribution system (H_2 mini-grid). Direct hydrogen PEM fuel cell power systems (FCPSs) utilizing H_2 mini-grids could improve reliability, cost, start-up time, emissions, and noise compared to reformate-based systems. In addition, producing hydrogen centrally for both vehicle fueling and FCPSs via a H_2 mini-grid provides an early market and fuel infrastructure for direct hydrogen vehicles.

In the metal hydride slurry mini-grid concept, reformate would be produced at a H_2 station, and hydrogen would be absorbed into the metal hydride slurry while impurities would be stripped out. Then, some of the metal hydride slurry would be pumped through pipelines to local buildings, where pure hydrogen would be desorbed and used to generate power in distributed FCPSs. The spent hydride slurry would then be pumped back to the H_2 station through a separate pipeline (perhaps concentric pipelines) for regeneration. Additional hydrogen capacity would be required at the H_2 station to meet vehicle fueling demands. This application has the potential advantages of being safer and requiring smaller pipe diameters than low pressure (~ 10 atm) cH_2 distribution. In addition, overall system efficiency could be improved provided the FCPSs supply some or all of the heat necessary to desorb hydrogen from the metal hydride.

Approach

In this phase of work, started in June 2002, we are evaluating the feasibility of using metal hydride slurries for purification and the potential benefits of using metal hydride slurries for hydrogen delivery via a H_2 mini-grid.

In order to assess the potential economic, environmental, and other benefits of using metal hydride slurries in the H_2 mini-grid application, we have constructed a FCPS performance model. Annual hourly building load profiles and fuel cell system efficiencies are used in the model to determine hydrogen requirements from the H_2 mini-grid and to optimize fuel cell size. In utility-connected buildings, grid power and natural gas demands are also determined, and annual energy costs are calculated based on utility rates and the cost of hydrogen from the H_2 mini-grid. Annual costs to the building owner and the cost of electricity (COE) are calculated based on the annual energy, maintenance, and capital costs of the FCPSs. Annual greenhouse gas and other emissions can also be determined based on the annual energy demand (i.e. hydrogen, natural gas, and grid electricity). The cost of hydrogen is calculated based on the capital cost of the H_2 mini-grid (i.e. distribution cost) plus the marginal cost of producing hydrogen at the H_2 station (i.e. marginal production cost). Alternatively, hydrogen can be priced at a premium to subsidize hydrogen sales to vehicles.

In order to evaluate the long-term feasibility of fluorinated metal hydride purification, we will perform molecular-level theoretical calculations using first principles and quantum modeling to understand the underlying microscopic mechanism of a fluorinated metal alloy (e.g. La-Ni-Al).

We will test two main hypotheses: (1) fluorination reduces the binding energy of undesired molecular species (e.g. O_2 and CO), and (2) the diffusion barrier created by the fluorinated surface is much lower for hydrogen molecules than for undesired molecules. Based on the calculations, we will generate a general model for surface protection of metal hydrides and formulate general principles for protection techniques. resis.

Results

A summary of our work in progress and some preliminary results and conclusions are presented here. The final results and conclusions will be detailed in a final report, expected to be completed in late fall 2003.

The National Fire Protection Agency (NFPA), the American Society of Mechanical Engineers (ASME), the Compressed Gas Association (CGA), the Code of Federal Regulations (CFR), the U.S. Department of Transportation (DOT), and industry experts were consulted for the design of the cH_2 mini-grid. We assume a delivery pressure equivalent to the output of the PSA (~ 10 atm) can be tolerated in most applications and no boost compressors are required over the short distribution distance (< 2 miles) of the H_2 mini-grid. We have estimated material, construction, "right-of-way", and "right of eminent domain" costs based on vendor quotes and additional cost assessments. Total capital cost for 4-inch pipe is estimated to vary between $250,000 and $600,000 per mile depending on location (rural, suburban, or urban). Right-of-way costs dominate in most cases.

Hourly electric and heat (space and water heating) load profiles for residential and commercial buildings in various locations have been generated for a typical meteorological year (TMY) using DOE EnergyPlus software. The load profiles are used in the FCPS performance model to calculate FCPS power demand (FCPS turns on when the building demand exceeds design power), cogen use (only when fuel cell is on and building heat is needed), and monthly utility demands. Example load profiles are shown in Figures 1 and 2. Note that the electric and space heating demands vary significantly from the winter to summer.

We constructed FCPS models using HYSYS process modeling software to evaluate system parameters that can affect system efficiency and cogen potential. The efficiency and cogen results are used in the FCPS performance model to calculate hydrogen (or natural gas) demand and actual cogen utilization. An example of a system level parametric analysis is shown in Figure 3. Note that low temperature and high pressure FCPS operation increases cogen capabilities because less heat is required for anode and cathode humidification. HYSYS models for the H_2 stations were developed in Phase I.

A FCPS performance model has been constructed using the building load profiles and FCPS efficiency and cogen calculations. The model calculates the FCPS and utility energy demands for every hour of a TMY for various building types. We have estimated preliminary annual costs for direct hydrogen and reformate-based FCPSs using the FCPS performance model with typical utility rates and estimates for hydrogen, FCPS capital, and maintenance costs. Examples of the annual cost

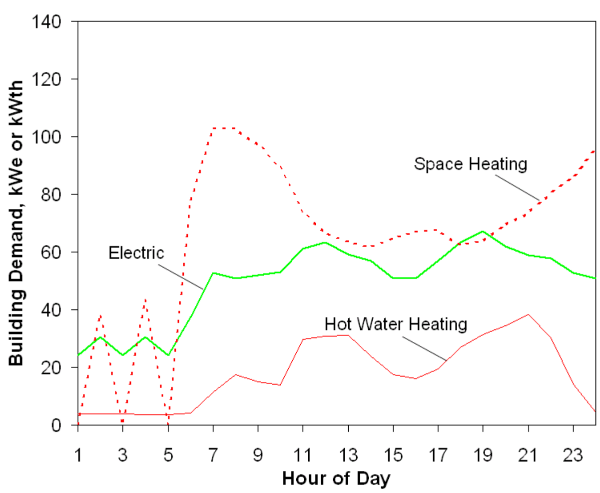

Figure 1. 24-Hour New York City Fast Food Restaurant Load Profile - Winter Day Example

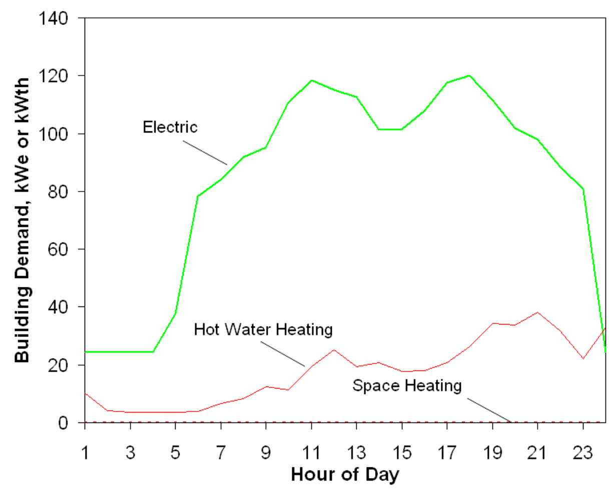

Figure 2. 24-Hour New York City Fast Food Restaurant Load Profile - Summer Day Example

FCPS Parameters	Base Case	Low Temp.	Low Voltage	Low H_2 Util.	High Press.
Temperature, °C	80	70	80	80	80
Design Voltage, V	0.70	0.70	0.63	0.70	0.70
Hydrogen Utilization, %	95	95	95	88	95
Pressure, atm	1.2	1.2	1.2	1.2	1.5
Preliminary Results					
Cogen Potential[1], kWth/kWe	0.68	0.81	0.87	0.87	0.87
System Efficiency[2], % (LHV)	49	49	44	45	48

[1] Cogen is reduced by humidification requirements.
[2] Includes 95% power electronics (i.e. inverter) efficiency, 95% hydrogen utilization, and parasitic loads.

Figure 3. Parametric Analysis using HYSYS Models - Direct Hydrogen FCPS Example

estimates are shown in Figures 4 and 5. Note that in Figure 4, smaller FCPSs suffer from poor economies of scale (more expensive capital on a $/kWe basis) and larger FCPSs suffer from low utilization.

The examples in Figures 4 and 5 assume the following:

- FCPS operates only when the building demand for power meets or exceeds the FCPS design power.
- Low-temperature cogen assumes the FCPS waste heat (i.e. cogen potential) can be used to meet some or all of the building hot water demand (61-74°C) when the FCPS is operating.
- High-temperature cogen assumes some or all of the hot water and space heating demands (74-94°C) can be met when the FCPS is operating.
- Utility stand-by charges are zero.
- The installed capital costs for 50-kWe direct hydrogen and reformate-based FCPSs are $24,500 and $44,500, respectively (assuming high volume manufacturing).
- FCPS stack and fuel processor catalyst bed lives are 40,000 hours.
- Hydrogen is sold to the building owner for just $1.00/kg, representing the marginal cost to produce hydrogen at the H_2 station. This does not include the cost of distribution through the H_2 mini-grid (work in progress).

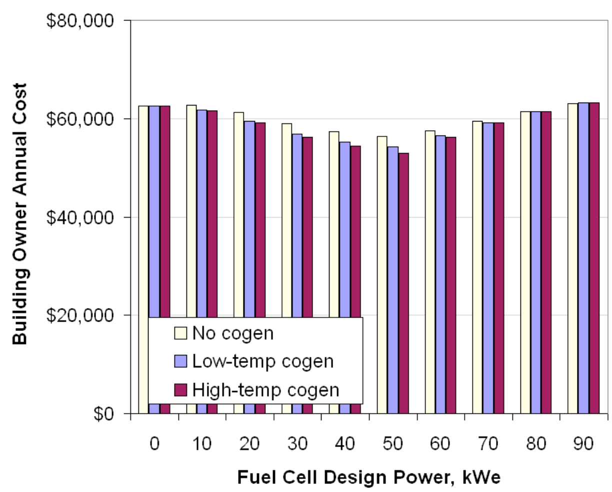

Figure 4. Preliminary FCPS Annual Costs with and without Cogen - Direct Hydrogen Example

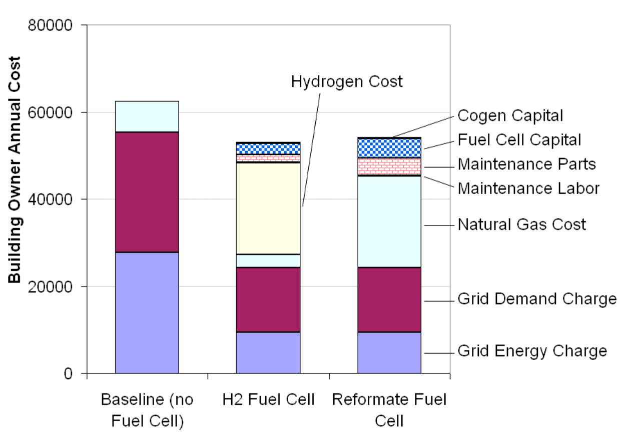

Figure 5. Preliminary FCPS Annual Cost Breakdown - 50 kWe with High-temp Cogen Example

Conclusions

Based on the preliminary results, a few observations can be made:

- There is an optimum FCPS size that will depend on the building load profile (i.e. utilization) and assumed economies of scale (see Figure 4).
- It is not clear whether cogen (high- or low-temperature) will be attractive for distributed FCPSs under the assumed mode of operation and load profiles used in this analysis to date (see Figure 4). The relatively small annual cost savings will have to be weighted against additional system complexity and reliability concerns.
- Fuel costs (hydrogen or natural gas) dominate the annual cost of the FCPSs, assuming capital and maintenance cost estimates for high volume manufacturing (see Figure 5).
- Hydrogen delivery will have to be relatively cheap to maintain competitiveness with reformate-based systems (see Figure 5). However, other benefits of the direct hydrogen FCPSs, such as improved reliability, quick start-up, and quiet and emissions free operation, have not been incorporated into the economic analysis to date.
- In the near-term, when capital and maintenance costs will be high, both direct hydrogen and reformate-based FCPSs will have difficulty competing with the utilities based on energy savings alone. Other benefits of FCPS distributed generation will have to be valued (e.g. power quality, reliability).

References

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